

## ALTERNATIVE FUELS FROM BIOMASS

Charles E. Wyman  
Alternative Fuels Division  
National Renewable Energy Laboratory  
1617 Cole Boulevard  
Golden, Colorado 80401

### ABSTRACT

Substitution of biofuels derived from cellulosic biomass for conventional fuels would reduce the accumulation of carbon dioxide in the atmosphere and the possibility of global climate change, improve our energy security and balance of trade deficit, revitalize the rural and farm economies, and address urban air pollution and waste disposal problems. The major fractions of biomass, cellulose and hemicellulose, can be broken down into sugars that can be fermented into ethanol. Through technology advances for producing ethanol, the projected cost at the plant gate has been reduced from about \$3.60/gallon ten years ago to \$1.27/gallon now, and opportunities have been identified to further drop the price to \$0.67/gallon, a price competitive with gasoline from oil at \$25/barrel, within ten years. Through anaerobic digestion, a consortium of bacteria can also break down cellulosic biomass to generate a medium-Btu gas that can be modified (or cleaned up), resulting in pipeline-quality methane. The cost of this methane has been reduced to about \$4.50/MBtu ( $10^6$  Btu) for municipal solid waste (MSW) feedstocks, and technology advances could drop the price to about \$2.00/MBtu. Algae could consume carbon dioxide from power plants and produce lipid oil that can be converted into a diesel fuel substitute. Projected costs for this biodiesel have dropped from almost \$18.00/gallon to about \$3.50/gallon now, with a target of \$1.00/gallon. Biomass can also be gasified to a mixture of carbon monoxide and hydrogen for catalytic conversion into methanol. Currently, methanol from biomass is projected to cost about \$0.85/gallon, and with improved technology, a cost of \$0.50/gallon could be realized. Catalytic processing of pyrolytic oils from biomass produces a mixture of olefins that can be reacted with alcohols to form ethers such as methyl tertiary butyl ether (MTBE) for use in reformulated gasoline, for reduction of emissions. Costs could be competitive today for olefins from MSW. Because biofuels technologies require little if any fossil fuel inputs, carbon is recycled through their use, reducing substantially the net amount of carbon dioxide released to the atmosphere.

## INTRODUCTION

The United States contributes about 25% of the carbon dioxide (CO<sub>2</sub>) released from fossil fuels to the atmosphere, with transportation fuels accounting for about 27% of that amount (1). Carbon dioxide is believed to be the most important greenhouse gas, trapping nearly 50% of the radiation that could lead to global climate change (2), and significant benefit would be gained by development of fuels that do not contribute to the buildup of CO<sub>2</sub> in the atmosphere. Because significant air pollution problems are attributed to gasoline and other conventional fuels, alternative transportation fuels are of particular interest for reducing carbon monoxide and smog in our cities.

In addition to concern about the effects of fuel use on the environment, the U.S. economy depends strongly on unstable sources of imported petroleum. As a result, the nation experienced several oil price shocks as foreign producers controlled supplies of oil in the 1970s. In 1990, the price of oil and gasoline increased again because of the Iraqi invasion of Kuwait, reminding us that oil and natural gas represent the weakest links in the U.S. energy supply. The United States imports about half of the petroleum it uses annually, and even though natural gas imports are now less than 6% of usage, gas and oil imports in the year 2000 are predicted to rise to 11% and 56% of the 23.6 and 37.2 quads of consumption, respectively. Furthermore, petroleum imports are responsible for about 40% of the trade deficit of the United States (3). About 97% of the energy consumed by the transportation sector is derived from petroleum, making this important segment of our economy particularly vulnerable to disruptions in unstable sources of oil.

Fuels known as biofuels can be produced from many plant materials and waste products such as agricultural wastes and municipal solid waste (MSW) that together are called biomass. Several oxygenated biofuels such as ethanol reduce carbon monoxide emissions when blended with gasoline. A number of biofuels can be substituted directly for conventional transportation fuels to reduce urban air pollution. Biofuels can also be used in the residential, industrial, and utility sectors. Substantial improvements have been made in the technology for producing the liquid and gaseous biofuels that this nation needs most, and these fuels now have the opportunity to make a strong impact on our fuels use.

This paper focuses on the progress of and prospects for promising biofuels produced by both biological and thermal reactions. First, the possible contribution of biofuels to our energy supply will be presented. Then, the technologies for producing biofuels will be summarized, and some of their important characteristics discussed. The potential benefits of biofuels for mediating CO<sub>2</sub> buildup will be illustrated.

## BIOFUELS PRODUCTION TECHNOLOGIES

### BIOMASS AVAILABILITY AND COST

Plants use the sun's energy to convert CO<sub>2</sub> and water into simple sugars through photosynthesis. These sugars can be stored directly in plants such as sugar cane or combined to form starch for plants such as corn. All plants join sugars together to form the structural carbohydrate polymers cellulose and hemicellulose, which together with lignin support the plant.

The cellulose, hemicellulose, and lignin components represent the largest fractions of plant matter and can be termed cellulosic biomass or just biomass. When we burn biomass, the stored energy from the sun is released. The energy content of biomass can also be thermally or biologically transformed to liquid or gaseous fuels that integrate well with our existing fuel distribution and use infrastructure.

Although the outward appearance of the various forms of cellulosic biomass such as wood, grasses, municipal solid waste (MSW), and agricultural residues is different, all of these materials are quite similar in composition. Cellulose is generally the dominant fraction, representing about 40% to 50% of the material by weight, while the hemicellulose portion represents 20% to 40% of the material. The remaining fraction is predominately lignin with lesser amounts of substances called extractives. The cellulose polymer is composed of glucose sugar while arabinose, mannose, xylose, glucose, and other sugars make up the hemicellulose. Although most forms of cellulosic biomass are low in cost, the historical costs of conversion to liquid and gaseous biofuels have been too high to allow economic application of these technologies on a large scale.

It is estimated that about 190 million acres of land could be used to grow energy crops dedicated for the production of biofuels. For an average productivity of 9 tons/acre/year, about 1.7 billion tons of cellulosic biomass could be harvested each year (4). If accessible underutilized wood, agricultural residues, and MSW are included, about 2.5 billion dry tons per year of cellulosic biomass could be produced at prices from \$18 to \$65 per dry ton (1,5,6). As a perspective on the size of this resource, about 250 billion gallons of liquid fuels could be produced from this quantity of biomass compared to the approximately 115 billion gallons of gasoline used in the United States.

## FUEL ETHANOL

More than 3 billion gallons of ethanol produced from sugar cane is used in Brazil each year. However, U.S. sugar prices are controlled at about \$0.20/pound, a price that is too high for fuel production. Instead, about 1 billion gallons of ethanol are made from corn in the United States each year. Ethanol from corn currently sells for about \$1.20 to \$1.30/gallon and is competitive with state and federal tax incentives. Ethanol blends from starch and sugar crops comprised as much as 8% of the U.S. gasoline market in 1987, up from less than 1% in 1981. There are about 50 U.S. fuel ethanol manufacturing facilities that use corn and other grains as feedstocks.

Over the years, several processes have been studied for conversion of cellulose-containing biomass to ethanol catalyzed by dilute acid, concentrated acid, or enzymes known as cellulases. In each option, the feedstock is pretreated to reduce its size and open up the structure. The cellulose fraction is hydrolyzed by acids or enzymes to produce glucose sugar, which is subsequently fermented to ethanol. The soluble xylose sugars derived from hemicellulose are fermented to ethanol as well, while the lignin fraction can be burned as fuel to power the rest of the process, converted into octane boosters, or used as a feedstock for production of chemicals.

Dilute acid systems typically have low ethanol yields of 50% to 70%. Concentrated sulfuric or halogen acid options achieve the high yields required, but the acids must be recovered

at a cost substantially lower than the cost at which these inexpensive materials are produced in the first place, a difficult requirement. Enzyme-catalyzed options provide the high yields of ethanol necessary for economic viability, under mild conditions, with low concentrations of enzyme. In addition, enzyme-catalyzed processes have tremendous potential for technology improvements that could bring the selling price of ethanol down to levels competitive with those of existing fuels. Enzymes are also biodegradable and environmentally benign. At this time, the simultaneous saccharification and fermentation (SSF) enzyme-based process has emerged as the favored route to achieve low-cost fuel ethanol production within a reasonable time frame (7).

In the SSF process, the cellulosic biomass is first pretreated to open up the biomass structure and facilitate subsequent processing. Several options have been considered for biomass pretreatment including steam explosion, acid catalyzed steam explosion, ammonia fiber explosion, and organosolv, but the dilute acid option appears to have the best near-term economic potential. In this process, about 0.5% sulfuric acid is added to the feedstock, and the mixture is heated to around 140° to 160° C for 5 to 20 minutes. Under these conditions, most of the hemicellulose is broken down to form xylose and other sugars, leaving behind a porous material of primarily cellulose and lignin that is more accessible to enzymatic attack.

Following pretreatment, a portion of the pretreated biomass is used in an enzyme production vessel to support growth of a fungus that produces cellulase enzyme. Then, the cellulase enzyme is added to the bulk of the pretreated substrate along with yeast or other fermentative microorganisms. The enzymes catalyze the breakdown of the cellulose by the so-called hydrolysis reaction to form glucose sugar; the yeast or other suitable microbe ferments the glucose to ethanol. The presence of yeast along with the enzymes minimizes sugar accumulation in the vessel, and since the glucose produced during breakdown of the cellulose slows down the action of the cellulase enzymes, higher rates, yields, and concentrations are possible by consuming the sugar as it is released. Additional benefits are that this process reduces the number of fermentation vessels and that the presence of ethanol makes the fermentation mixture less likely to be invaded by unwanted microorganisms. Finally, the ethanol is separated from the rest of the fermentation broth in a purification step.

The xylose and other sugars released from the hemicellulose polymers are often predominantly five-carbon sugars that are not as readily converted to ethanol as glucose, and until recently, these sugars had to be discarded. However, several options have been developed for using xylose. At this time, the most promising option appears to be the use of genetically engineered bacteria (8,9) or some new yeast strains for ethanol production.

Because lignin represents a significant fraction of cellulosic biomass, it is important to derive value from lignin. Lignin has a high energy content and can be used as a boiler fuel. Generally, the amount of lignin in most feedstocks is more than sufficient to supply all the heat and electricity required for the overall ethanol production process, as well as to generate excess heat or electricity. Thus, additional revenue can be generated from electricity exports from the plant (10). The electricity sold for current plant designs is equivalent to about 8% to 10% of the Btu value of the ethanol product, and greater revenues are likely as the technology is improved to require less process heat and electricity. Alternatively, lignin could be converted into chemicals or octane boosters such as methyl aryl ethers.

Progress on the enzyme-catalyzed processes to convert cellulosic biomass into fuel ethanol has been substantial over the last ten years, with projected selling prices dropping from about \$3.60/gallon in 1980 (11) to only about \$1.27/gallon now (12). This selling price reduction is due to improvements in enzymes to achieve higher rates, yields, and concentrations with lower loadings, proper selection of fermentative microbes, and advances in xylose fermentations through genetic engineering.

Significant opportunities still exist to lower the selling price of ethanol from cellulosic biomass at the plant gate to \$0.67/gallon. Key target areas include improved glucose and xylose yields from pretreatment, increased ethanol yields to 90% or greater from cellulose and xylose fermentations, decreased stirring and pretreatment power requirements, better productivities through continuous processing, low-cost production of octane enhancers or chemicals from lignin, increased ethanol concentrations, and reduction of fermentation times. Feedstock costs are a significant fraction of the final product selling price, so improvements in feedstock production, collection, and genetics could provide additional cost reductions through economies of scale for larger ethanol plants, decreased feedstock costs, and less non-fermentable feedstock. Many of these goals have been met individually and the evidence that the rest can be achieved is great; the primary need is to meet them simultaneously. Fortunately, there are enough options for lowering the selling price of ethanol so that not all the technical goals must be achieved to reach the target.

## BIODIESEL FROM MICROALGAE

Microalgae are single-celled plants that contain photosynthetic machinery driven by the sun's energy to combine  $\text{CO}_2$  and water to form a variety of products. Algae are particularly unique in their ability to produce a high fraction of their total weight (about 60% or more) as lipid oils or triglycerides. Lipids are hydrocarbons with a higher energy density than that of the carbohydrates plants typically produce. Although these algal oils can be used directly in diesel engines, they can also be readily converted into esters that more closely match diesel fuel properties and burn more cleanly (13). Diesel fuel currently supplies about 17% of the energy used for transportation in the United States. Production of diesel fuel from algae complements ethanol manufacture from cellulosic biomass in that as ethanol displaces the fraction of petroleum converted into gasoline, substitutes must be found for the fraction now used to manufacture diesel fuel.

Microalgae grow well over a wide range of temperatures in high-salinity water that is unsuitable for other purposes. Therefore, it may be possible to use the abundant high-salinity water in aquifers coupled with inexpensive flat land available in the Desert Southwest to grow microalgae to produce biodiesel. Shallow uncovered ponds or raceways could be created to produce algae with slowly rotating paddle wheels used to circulate the water and provide mixing. Carbon dioxide from power plant flue gas would be injected into the ponds to promote algal growth. The rapidly growing microalgae would be harvested, and the lipid oils would be extracted for conversion into ester fuels (13).

Microalgal ponds are very efficient in their uptake of  $\text{CO}_2$ , recovering about 90% of the gas injected into a pond. Thus, they provide an effective means of  $\text{CO}_2$  recovery from power plants. Of course, when ester fuels are burned, the  $\text{CO}_2$  captured by the algae is released to the

atmosphere, but almost twice as much energy is produced for a given amount of CO<sub>2</sub> released as would be possible without the use of algal ponds. As a result, a coal-burning power plant coupled to an algal pond would contribute far less CO<sub>2</sub> to the atmosphere than a conventional gas-fired plant on a total energy released basis (14). Of course, similar benefits could be provided to a gas-fired power plant. If the lipid oils were converted to a chemical for production of durable goods, the carbon could be sequestered for a longer term, reducing the impact of fossil fuel use on CO<sub>2</sub> accumulation. Use of biodiesel also has a low sulfur impact on the environment.

Progress on technology for producing oil from microalgae has been considerable. A number of strains have been collected that are tolerant to high salinity, high light intensity, wide temperature variations, and extreme temperatures. Many of these strains grow rapidly and produce about 60% of their weight as lipids when they are deprived of key nutrients such as silicon for diatoms or nitrogen for green algae (15). The enzyme acetyl Co-A carboxylase (ACC) has been identified as a key catalyst in lipid oil synthesis (15,16), and research is now focused on developing techniques to genetically enhance lipid oil synthesis by controlling the genes responsible for ACC production.

The projected price of biodiesel production from algae has dropped from approximately \$18/gallon in the early 1980s to around \$3.50/gallon now. Opportunities have been identified to reduce the price to about \$1.00/gallon. The primary need is to enhance the growth rate of algae while achieving high lipid oil concentrations. However, these estimates are based on commercial prices for CO<sub>2</sub>, which represents a major share of the oil production cost. If fines were levied for CO<sub>2</sub> releases into the atmosphere, CO<sub>2</sub> prices would drop drastically or users might be paid to accept this gas, and algal oil production could be cost competitive much sooner.

## BIOGAS

Natural gas, which is primarily methane, is considered an environmentally clean and economically attractive fuel with a high energy content. It is widely used for industrial, residential, and utility applications. It also has potential merit for transportation markets, but it is nonrenewable. Biogas, a mixture of approximately equal portions of methane and CO<sub>2</sub>, is a medium-Btu gas formed by a biological process called anaerobic digestion, in which complex organic compounds are decomposed by microorganisms. Anaerobic digestion has been used in the United States since early in the twentieth century to stabilize and reduce the volume of municipal sludge before disposal. In typical installations, the biogas produced in the process was flared rather than recovered as an energy source. Anaerobic digestion is also used to remove soluble wastes from chemical plant effluents. However, although the anaerobic digestion processes now operating are effective in meeting waste disposal requirements, current systems were not designed for cost-effective energy production and are not well suited to utilization of solid cellulosic biomass. In sanitary landfills, naturally occurring anaerobic bacteria break down the biodegradable fraction of the MSW buried there to form biogas although the gas production rates and yields vary widely. Only a small percentage of that gas is now being economically recovered.

In the anaerobic digestion process, one group of bacteria breaks down cellulose and other complex molecules enzymatically into simple sugars and other monomers. Then, other types of

bacteria digest these products, producing organic acids that are in turn broken down to form still smaller molecules of acetate, formate, hydrogen, and CO<sub>2</sub>. Finally, specialized bacteria, called methanogens, use these compounds to produce methane and CO<sub>2</sub>. When CO<sub>2</sub> is removed from biogas, the methane-rich product is a high-Btu gas that can be directly substituted for natural gas. Thus, this biological pathway directly converts organic matter into a gas that can be used directly in a boiler or processed to be compatible with the existing distribution infrastructure.

If MSW is employed as the substrate, anaerobic digestion also provides an environmentally sound disposal method. In the anaerobic digestion of MSW, the solid waste is shredded and ferrous materials are removed. Generally, it is also necessary to separate the extra-fine and oversized materials for landfill disposal. The mixture is fed into digesters, and the microbial process converts about half the solid waste into a gas composed of about equal fractions of methane and CO<sub>2</sub>. The solids left after digestion is complete are dewatered for disposal. For a tipping fee of \$20/ton for the MSW processed, a methane selling price of about \$4.50/MBtu (10<sup>6</sup> Btu) is estimated for established technology.

Several improvements have been made in the anaerobic digestion process. Stratified operation of the digester can result in higher solids concentrations and achieve 10% higher methane yield than a conventional vessel. Technology has also been demonstrated to enrich the methane content of the product gas from an anaerobic digester to near pipeline quality by recirculating a leachate stream from the digester through an air stripping unit or other CO<sub>2</sub> desorption process. Novel anaerobic digestion units have been operated at 35% to 40% solids concentrations with gas generation rates of 7 to 9 times those possible with conventional devices, which are limited to 6% to 10% solids levels (17). Such devices reduce the volume of the containment vessel and thus decrease vessel costs per amount of methane generated.

Continued research could result in further reductions in methane cost to approximately \$2.00/MBtu (18). Research is needed to identify the organisms present in anaerobic digesters and clarify their complex interactions. Specific organisms can then be selected for genetic breeding and manipulation to allow operation of anaerobic digesters at optimal conditions. Feedback and control mechanisms should be developed to maintain stable operation of digesters (19). Engineering efforts should be undertaken to develop large-scale reactor designs that can process high concentrations of solids to decrease the cost of biogas production. Work is also needed on landfill gas recovery to understand the effect of atmospheric conditions on gas flow, evaluate microbial populations that produce landfill gas, and improve gas generation and capture methods.

## METHANOL FROM BIOMASS

Biomass can be thermally gasified to produce synthesis gas (syngas) rich in carbon monoxide and hydrogen; the syngas can then be catalytically converted to methanol. Methanol production includes steps for feed preparation, thermal gasification, methanol synthesis, and gas conditioning and cleanup. Feed preparation typically employs well developed equipment for biomass drying, size reduction, and feeding. Methanol synthesis from carbon monoxide and hydrogen is a well established technology. In order to achieve commercial application of methanol production from biomass, we need to develop low-cost technology for gasifying the

biomass to carbon monoxide and hydrogen and preparing the gas stream for catalytic formation of methanol.

The gasification step can be carried out by controlled direct addition of air or oxygen to the gasifier to produce heat and drive the breakdown of biomass to form carbon monoxide and hydrogen. In such processes, part of the biomass is burned to provide the heat required to drive the formation of the target gases. Alternatively, indirectly heated gasifiers rely on transfer of heat from an external source through a heat exchange device to break down biomass (20,21). Indirect gasifiers may have some cost advantages relative to units that are directly fed air or oxygen. However, further engineering evaluations and economic studies are needed to establish the relative merits of the alternative processes.

Although the raw syngas is rich in carbon monoxide and hydrogen, it cannot be directly processed in the catalytic synthesis unit because it contains significant amounts of impurities including particulate matter, methane, tar, and various light hydrocarbons. In addition, the ratio of carbon monoxide to hydrogen must be adjusted to that required for methanol synthesis. Research has shown that the gas can be cleaned up and the composition adjusted for methanol synthesis. However, further work is required to determine the fate of organic impurities and methane; establish the effect of hydrogen, carbon monoxide, and  $\text{CO}_2$  on tar and methane removal; estimate useful catalyst life; and demonstrate the ability of catalysts to destroy tars and reduce methane under realistic operating conditions with various feedstocks.

Currently, methanol is estimated to cost about \$0.85/gallon from biomass feedstocks costing about \$42/ton. Several opportunities have been identified that would make methanol from biomass competitive with gasoline as a neat fuel. Direct syngas conditioning in one step would replace expensive quenching and scrubbing operations to remove tars and subsequent reheating and steam reforming to reduce excessive levels of methane. We need to develop catalysts that meet lifetime requirements, as well as better gas cleanup systems. Concepts must also be tested at a reasonable scale to establish operational parameters and commercial potential. Improvements in feedstock costs, as discussed for ethanol production, would also benefit methanol economics. Successful demonstration of these improvements could drop the cost of methanol to about \$0.50/gallon, a price competitive with gasoline from oil at \$25/barrel.

## REFORMULATED GASOLINE COMPONENTS (RGCs)

Concerns about urban air pollution have led to enactment of legislation such as the Clean Air Act Amendments of 1990, which require measures be taken to improve air quality. Use of neat fuels such as ethanol and methanol are one way to reduce emissions of unburned hydrocarbons and carbon monoxide, which contribute to smog formation. In addition, gasoline compositions are being changed or "reformulated" to reduce their contribution to air pollution. Oxygenates such as ethanol and ethers are added to gasoline to improve fuel combustion and reduce the release of smog-forming compounds as well as carbon monoxide. The Clean Air Act Amendments of 1990 mandate the use of 2.7% oxygen in fuels used in several ozone and carbon monoxide non-attainment regions, thus causing a large demand for oxygenates such as ethanol and methyl tertiary butyl ether (MTBE). Ethers such as MTBE and ethyl tertiary butyl ether (ETBE) are made by reacting the appropriate alcohol (i.e., methanol or ethanol, respectively) with



isobutylene. Currently, isobutylene is derived from fossil sources, but these compounds can also be made by fast pyrolysis of biomass followed by catalytic reaction of the pyrolysis products to form olefins. The olefins in turn can be reacted with alcohols to form RGCs such as ETBE and MTBE.

Fast pyrolysis rapidly heats the biomass to temperatures at which the predominant pyrolysis reactions form oxygenated crude oil vapors, rather than char, water, or gases. A vortex reactor forces biomass particles to slide along the externally heated reactor wall, and the close contact between the particles and the wall produces high rates of heat transfer. As a result, the surface of the biomass particle is pyrolyzed and removed, but the bulk of the particle is still unheated through an ablative pyrolysis phenomena (22,23).

The oxygenated crude pyrolysis oil vapors produced in the vortex reactor are converted into olefins and other products through a thermal cracking operation. Extensive studies of these reactions have typically shown that some olefins and other hydrocarbons of interest result but in yields that are not high enough to be economically interesting. However, zeolite catalysts such as HZSM-5 used to convert methanol to gasoline crack the pyrolysis oil vapors with dramatically higher olefins production. Researchers have identified operating conditions with this catalyst in a slipstream reactor, and low coke yields and relatively high yields of high-octane alkylated aromatics and gaseous olefins were achieved. These products give a very high octane blending stock for use with reformulated gasoline (23,24).

The offgas from the catalytic cracking reactor contains a considerable amount of gaseous olefins. Catalytic conversion of these olefins to larger hydrocarbon molecules has been studied in a secondary catalytic reactor to facilitate condensation and recovery of these materials. A compressor pressurizes the gases that enter the secondary catalytic reactor. Primarily isoparaffins boiling in the gasoline range have been generated from the gaseous olefins. Changes in the catalysts, coreactants, temperatures, and pressures selected could change the products from the secondary reactor.

Preliminary evaluations of the economics of the combined pyrolysis and catalytic conversion process are encouraging, especially when refuse-derived fuel (RDF), a low-cost feedstock derived from MSW that gives enhanced yields of olefins compared to those from wood, is used as the feedstock. Research on novel catalysts will increase both the olefin yields and the selectivity toward olefins versus aromatics. Initial catalyst screening in the laboratory has already identified some promising candidates, and the results suggest that yields could be improved substantially.

Preliminary process evaluations of the advanced catalytic process suggest that mixed ethers could be produced for \$0.67/gal while they would cost about \$0.96/gal based on existing technology (25). However, the vortex reactor represents a new technology, which carries a considerable risk because of the lack of current industrial experience. Therefore, further research is required in areas such as selectivity and catalyst life. In addition, the ability to scale up the fast pyrolysis of biomass to produce condensable pyrolysis vapors must be demonstrated.

## IMPACT OF BIOFUELS ON CARBON DIOXIDE ACCUMULATION

In this section, the impact of using biofuels on CO<sub>2</sub> accumulation and the potential for global climate change will be discussed. An example will be presented based on ethanol production from cellulosic biomass, but the concepts presented are applicable to any of the biofuels that have been presented here.

Carbon dioxide released during fermentation and ethanol combustion is recycled back to grow new biomass, replenishing that harvested for ethanol manufacture. In addition, the lignin in the feedstock can be burned to provide all the process heat and electricity needed to drive the conversion process, and some heat or electricity is left to sell for added revenue. Thus, provided new trees or other biomass are planted to replace those that are harvested for energy, CO<sub>2</sub> provides the key link between the fuel and the biomass resource, and CO<sub>2</sub> does not accumulate in the atmosphere. Fossil fuels used in the production and transport of the biomass and the ethanol are the only sources that can lead to CO<sub>2</sub> accumulation.

Considerable controversy and confusion exists about the amount of fossil energy required to produce ethanol and the interpretation of this information for energy efficiency and the impact on potential global climate change. Energy inputs must be properly accounted for and the performance of ethanol must be properly compared to that for fossil fuels if comparisons are to be made between fuels.

### ENERGY USE

Figure 1 summarizes energy flows for the production of ethanol from cellulosic biomass (1). Modest energy inputs are required to produce cellulosic biomass because cultivation and

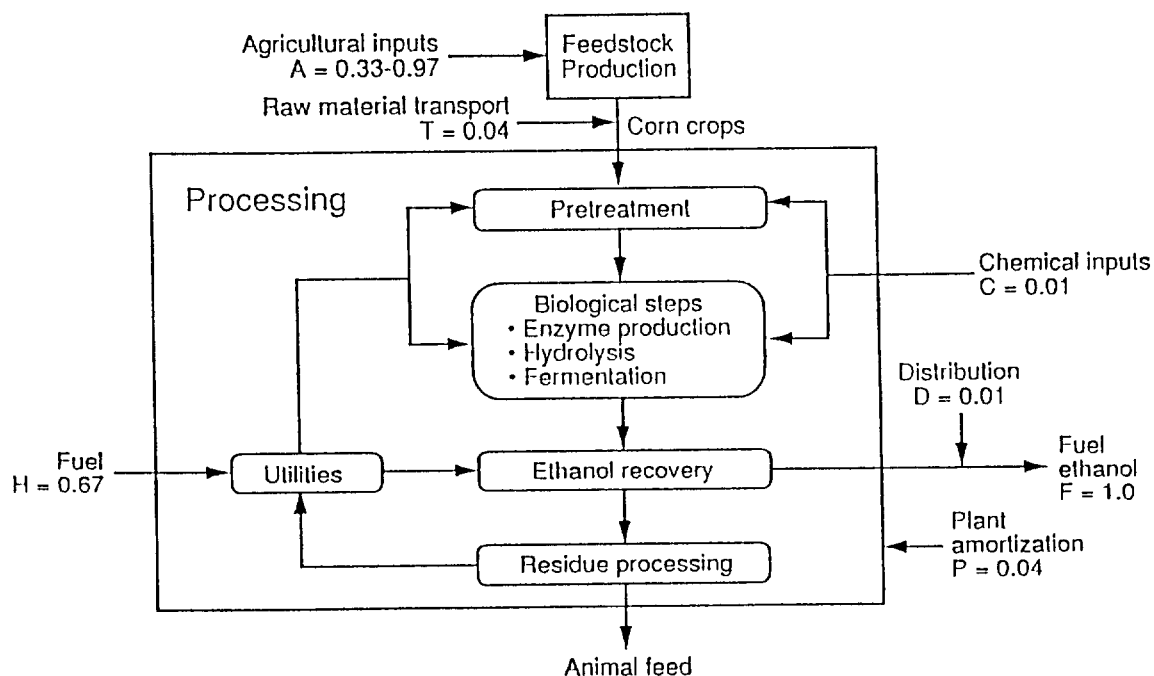


Figure 1. Energy requirements and outputs for production of ethanol from cellulosic biomass based on one unit of ethanol energy output

fertilizer needs are not large. In addition, no process energy input is shown because the lignin contained in the feedstock can be used as a boiler fuel, and the amount of energy contained in the lignin is sufficient to produce process heat and electricity for the overall process. In addition, the equivalent of 8% of the ethanol fuel value can be sold as electricity (9), thereby displacing about 3 times that amount of fossil energy inputs for electricity production by power companies.

If we add the total amount of fossil energy inputs, about 19,000 Btu/gallon of ethanol are required for ethanol production from cellulosic biomass. Alternatively, 3 times the electricity produced could be subtracted from the fossil fuel requirements to account for the fossil fuel that would be used in any event for producing that quantity of electricity (26). In this case, the net amount of fossil fuel use, as shown in Table 1, is only about 800 Btu/gallon of ethanol. For comparison, production of gasoline requires about 14,000 Btu/gallon of gasoline produced. Gasoline has a lower heating value of about 115,000 Btu/gallon, compared to ethanol at 76,000 Btu/gallon.

## CARBON DIOXIDE RELEASED

An estimate of the contribution of ethanol production to CO<sub>2</sub> accumulation in the atmosphere can be performed by weighing the quantities of fossil fuels used according to the amount of CO<sub>2</sub> released by each. For the purposes of this discussion and with reference to Figure 1, natural gas is assumed to be the fuel source for agricultural (A), chemical (C), and plant amortization (P) inputs; petroleum is assumed for transportation (T) and distribution (D). Combining CO<sub>2</sub> release data for these sources with the energy requirements presented in Figure 1 gives the results presented in Table 1 for ethanol derived from cellulosic biomass. Only CO<sub>2</sub> is included that is produced by combustion of fossil fuels since CO<sub>2</sub> generated during fermentation of biomass cellulose and hemicellulose and combustion of lignin and ethanol can be recycled to grow new biomass to replace that harvested for energy production.

It is interesting to note that if the fossil equivalent for production of electricity is subtracted from the fossil fuel sources for ethanol production from cellulosic biomass, a negative CO<sub>2</sub> contribution results (Table 1). This outcome is due to the low usage of fossil fuels for conversion of cellulosic biomass to ethanol and the displacement of electricity in the grid. To produce an equivalent amount of electricity from fossil resources such as coal would actually consume more fossil fuel than the total required for ethanol production, and subtracting the amount of CO<sub>2</sub> that would have been released anyway for generation of that quantity of electricity gives a net credit of 2 pounds of CO<sub>2</sub>/gallon of ethanol produced.

From the data in Table 1, it appears that production of ethanol from cellulosic biomass would be a minor contributor of CO<sub>2</sub> to the atmosphere. This is because all of the process heat is produced by combustion of lignin, a renewable feedstock. In addition, few fossil fuel inputs are needed to produce cellulosic biomass. Biomass sources of fuels and fertilizers could be substituted for the fossil fuels assumed in this analysis, resulting in no net CO<sub>2</sub> release for ethanol from cellulosic biomass. By way of comparison, gasoline use releases a total of 190 pounds of CO<sub>2</sub>/MBtu or 21.8 pounds/gallon of gasoline.

TABLE 1. CARBON DIOXIDE RELEASED IN ETHANOL PRODUCTION FROM CELLULOSIC BIOMASS

Process	Feedstock Production	Raw Material Transport	Chemical Inputs	Process Energy	Plant Amortiza- tion	Fuel Distribu- tion	Total Fossil CO <sub>2</sub>	Coproduct Displacement of CO <sub>2</sub>	Net Fossil CO <sub>2</sub>
Assumed Fossil Fuel	Natural Gas	Petroleum	Natural Gas	None	Natural Gas	Petroleum	--	--	--
Btu/Gallon Ethanol	11,400	3,000	800	--	3,000	800	19,000	(18,200)	800
Carbon Dioxide Released lb/gallon	1.5	0.5	0.1	--	0.4	0.1	2.6	(4.6)	(2.0)

Note: Calculated on the basis of the exported electricity displacing coal-generated electricity, which was generated at 33% efficiency

## FUEL UTILIZATION

In the United States, ethanol is currently blended with gasoline at 10% concentrations. As mentioned earlier, the energy content of ethanol is 76,000 Btu/gallon; gasoline contains about 50% more energy at 115,000 Btu/gallon. By accounting for each of these components, the energy content of the blend is about 111,000 Btu/gallon. If we assume that the range of a vehicle is proportional to the energy density of the fuel, then 1.036 gallons of blend would be required to travel the same distance as one gallon of gasoline. On the other hand, data from Southwest Research Institute have shown that there is no statistically significant difference in the mileage for a 10% blend versus that of regular gasoline. In effect, this evidence suggests that the ethanol blended with gasoline has an energy density equivalent to 115,000 Btu/gallon.

Use of neat ethanol can also be considered in at least two different ways. First, the amount of one fuel needed to travel the same distance as for another fuel can be determined by the ratio of the lower heating values of the two fuels. Thus, about 50% more ethanol would be required than for gasoline to give the same service. For an engine designed for gasoline use with only modifications in timing and air:fuel ratio to allow combustion of ethanol, ethanol fuel would give such a range. However, because ethanol has more favorable fuel properties such as a higher octane and heat of vaporization than gasoline, an engine optimized for ethanol can be 20% to 30% more efficient than a gasoline engine (1,6). Assuming the latter results in a ethanol driving range of about 80% of that of gasoline.

## COMPARISONS OF FOSSIL FUEL USE AND CARBON DIOXIDE RELEASE

Table 2 presents a comparison of the fossil fuel requirements for ethanol from cellulosic biomass and gasoline. Consideration is given to both blends and neat fuel use and to comparison of the amount of ethanol required based on lower heating value and performance. The lower end of the range shown is with credit given for fossil fuel displacement for electricity production, while the higher end does not account for excess electricity production. Blends of ethanol from cellulosic biomass with gasoline always yield lower fossil fuel use than gasoline. Furthermore, for neat fuel markets, ethanol production from cellulosic biomass requires one-fifth or less fossil fuel input than gasoline, depending on the accounting given for electricity production and the assumed efficiency of ethanol utilization.

Also presented in Table 2 is the amount of CO<sub>2</sub> released when a vehicle is propelled the same distance by ethanol as gasoline. Again, based on the low use of fossil fuels in production of ethanol from cellulosic biomass, this fuel scores very well in minimizing CO<sub>2</sub> emissions that could contribute to global climate change. If we subtract the CO<sub>2</sub> emissions that would have resulted from fossil fuels to generate the amount of electrical energy produced in the ethanol plant, the net effect is that ethanol removes CO<sub>2</sub>. It may be more appropriate to assign the CO<sub>2</sub> released to both electricity and ethanol based on the relative energy contributions and compare each to the alternative, but the benefits would still be substantial.

TABLE 2. FOSSIL FUEL USE AND CO<sub>2</sub> RELEASED FROM CELLULOSIC BIOMASS

Form of Fuel Use	Fossil Fuel Used (Btu/gal of gasoline equivalent)	CO <sub>2</sub> Released (lb CO <sub>2</sub> /gal of gasoline equivalent)
<b>Blends Based on Lower Heating Value</b>		
Ethanol	120,400 - 122,200	20.1 - 20.6
<b>Blends at Same Range as Gasoline</b>		
Ethanol	116,200 - 118,000	19.4 - 19.9
<b>Neat Fuel Based on Lower Heating Value</b>		
Ethanol	1,200 - 28,700	-3.0 - 3.9
<b>Neat Fuel Based on Improved Efficiency</b>		
Ethanol	1,000 - 23,800	-2.5 - 3.2
Gasoline	29,000	21.8

## CONCLUSIONS

A wide range of fuel products, which can reduce our vulnerability to disruptions in fuel supplies and improve our balance of trade deficit, can be produced from biomass, a renewable, abundant feedstock. These products include ethanol, methanol, methane gas, biodiesel, and olefins for production of RGCs. All of these biofuels can be used in the transportation sector, some as gasoline additives to reduce emissions of carbon monoxide and smog-forming compounds and others as substitutes for fossil fuels. Some can also be employed for residential, utility, and industrial applications. Substantial progress has been made in reducing the price of biofuels production, and goals have been defined to further reduce that cost. Many of these fuels are now ready for introduction into our energy sector for selected applications, and their use would improve our environment significantly from a viewpoint of both local air pollution and the potential for global climate change. Because only modest amounts of fossil fuels would typically be used to produce biofuels, the net release of CO<sub>2</sub> to the atmosphere would be small. Furthermore, for cellulosic biomass, all of the energy inputs in the overall process could ultimately be derived from renewable feedstocks, thereby avoiding any dependence on imported oil.

The work reported is funded by the Biofuels Systems Division of the U.S. Department of Energy. The work described in this paper was not funded by the U.S. Environmental Protection Agency and therefore the contents do not necessarily reflect the views of the Agency and no official endorsement should be inferred.

## REFERENCES

1. Lynd, L.R., Cushman, J.H., Nichols, R.J., and Wyman, C.E. Fuel ethanol from cellulosic biomass. *Science*. 251:1318, 1991.
2. Intergovernmental Panel on Climate Change. J.T. Houghton, G.J. Jenkins, and J.J. Ephraums, eds. *Climate Change—the IPCC Scientific Assessment*, Cambridge University Press, Cambridge, United Kingdom, 1990.
3. Wald, M.I. Greater reliance on foreign oil feared as U.S. output tumbles. *New York Times*. 18 January 1990.
4. National Renewable Energy Laboratory (Interlaboratory Report). *The Potential of Renewable Energy: An Interlaboratory White Paper*, SERI/TP-260-3674, National Renewable Energy Laboratory, Golden, Colorado, 1990.
5. Wyman, C.E., and Hinman, N.D. Ethanol: fundamentals of production from renewable feedstocks and use as a transportation fuel. *Appl. Biochem. Biotechnol.* 24/25:735, 1990.
6. Lynd, L.R. Production of ethanol from lignocellulose using thermophilic bacteria: critical evaluation and review. *Adv. in Biochem. Eng./Biotechnol.* 38:1, 1989.
7. Wright, J.D., Wyman, C.E., and Grohmann, K. Simultaneous saccharification and fermentation of lignocellulose: process evaluation. *Appl. Biochem. Biotechnol.* 18:75, 1988.
8. Ingram, I.O., Conway, T., Clark, D.P., Sewell, G.W., and Preston, J.F. Genetic engineering of ethanol production in *Escherichia coli*. *Appl. Environ. Microbiol.* 53(10):2420, 1987.
9. Ingram, I.O., and Conway, T. Expression of different levels of ethanologenic enzymes from *Zymomonas mobilis* in recombinant strains of *Escherichia coli*. *Appl. Environ. Microbiol.* 54(2):397, 1988.
10. Hinman, N.D., Schell, D.J., Riley, C.J., Bergeron, P.W., Walter, P.J. Preliminary estimate of the cost of ethanol production for SSF technology. *Appl. Biochem. Biotechnol.* 34/35:639 (1992).
11. Wright, J.D. Ethanol from lignocellulose: an overview. *Ener. Prog.* 8(2):71, 1988.
12. Chem Systems. *Technical and Economic Evaluation: Wood to Ethanol Process*, Chem Systems, Tarrytown, New York, prepared for the Solar Energy Research Institute, August 1990.
13. Neenan, B., Feinberg, D., Hill, A., McIntosh, R., Terry, K. *Fuels from Microalgae: Technology Status, Potential, and Research Requirements*. Solar Energy Research Institute, Golden, Colorado, 1986.
14. Chelf, P., Brown, L., and Wyman, C. Aquatic biomass resources and carbon dioxide trapping. Reprint from Proceedings of Electric Power Research Institute conference entitled "1990 Conference on Biomass for Utility Applications," Oct. 23-25, 1991, Tampa, FL.
15. Roessler, P. Changes in the activities of various lipid and carbohydrate biosynthetic enzymes in the diatom *Cyclotella cryptica* in response to silicon deficiency. *Arch. Biochem. Biophys.* 267:521, 1988.
16. Roessler, P. Environmental control of glycerolipid metabolism in microalgae: commercial implications and future research directions. *J. Phycol.* 26:393, 1990.

17. Rivard, C., Himmel, M., Vinzant, T., Adney, W., Wyman, C., Grohmann, K. Development of a novel laboratory scale high solids reactor for anaerobic Digestion of processed municipal solid wastes for the production of methane. *Appl. Biochem. Biotechnol.* 20/21:461, 1989.
18. Legrand, R., and Todd, T. *Systems Analysis of Municipal Solid Waste Biogasification*. Prepared for the Solar Energy Research Institute, Reynolds, Smith, and Hills, Inc., Jacksonville, Florida, 1990.
19. Chynoweth, D., Fannin, K., Jerger, D., Srivastava, V., Biljetina, R. *Anaerobic Digestion of Biomass: Status Summary and R&D Needs/1983*. Prepared for the Gas Research Institute, Chicago, Illinois, Institute of Gas Technology IIT Center, 1984.
20. Chem Systems. *Assessment of Cost of Production of Methanol from Biomass*, report DOE/PE-0097P, Chem Systems, Tarrytown, New York, December 1990.
21. Bain, R. Methanol from biomass: assessment of production costs. Presented at the November 1989 Hawaii Natural Energy Institute Renewable Transportation Alternatives Workshop, Honolulu, Hawaii, 1991.
22. Diebold, J., and Scahill, J. Biomass to gasoline. Upgrading pyrolysis vapors to aromatic gasoline with zeolite catalysis at atmospheric pressure. *Pyrolysis Oils from Biomass: Producing, Analyzing, and Upgrading*, E.J. Soltes and T.A. Milne, eds., American Chemical Society (ACS) Symposium Series 376, American Chemical Society, Washington, DC, 264-76, 1988.
23. Diebold, J., and Power, A. Data from International Energy Agency sponsored "Research in Thermochemical Biomass Conversion," 1988.
24. Evans, R., and Milne, T. Molecular beam, mass-spectrometric studies of wood vapor and model compounds over an HZSM-5 catalyst. *Pyrolysis Oils from Biomass: Producing, Analyzing, and Upgrading*, E.J. Soltes and T.A. Milne, eds., American Chemical Society (ACS) Symposium Series 376, American Chemical Society, Washington, DC, 311-27, 1988.
25. Overend, R. Thermochemical conversion technology. *In Proceedings of the Annual Automotive Technology Development Contractor's Coordination Meeting 1991*. Society of Automotive Engineers, Inc., Warrendale, Pennsylvania, 779, 1991.
26. Ho, S.P. Global impact of ethanol versus gasoline. Presented at the 1989 National Conference on Clean Air Issues and America's Motor Fuel Business, Washington, DC, 1989.